

Debromination of PBDEs in DE-83TM Technical Mix by electrolysis.

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1.0 Introduction

Two commercial mixtures of brominated flame retardants (BFRs), known as pentaBDE and octaBDE, have recently been phased out in the European Union and voluntarily phased out in the US due to increasing concerns over their persistence, bioaccumulation and potential toxicity.^{1,2} However, commercial mixtures based on decabromodiphenyl ether (DecaBDE) are still considered to be safe and are being used in flame retardation of high impact polystyrene, polyester fiber, coatings for automobile fabrics and acrylonitrile-butadiene-rubber.

The major component in DecaBDE, BDE-209, has been found in the environment.^{1,3} There is concern that BDE-209 is susceptible to degradation leading to the formation of lower brominated BDE congeners that are potentially more toxic to environmental species and to human health. Potential degradation pathways for BDE-209 in the environment include photolysis and metabolism. Photodegradation studies have been carried out and include homogeneous^{4,5} and heterogeneous^{6,7} solar photolyses of BDE-209, irradiation with artificial UV light^{4,8} and the photooxidation of polypropylene flame-retarded with DecaBDE.⁹ The products of BDE-209 photodegradation are lower brominated diphenyl ethers, and one report¹⁰ indicates that photolysis of the Octa-mix forms brominated dibenzofurans. The mechanism of photolysis may proceed either by reductive debromination or by photoinduced electron transfer. It would be expected that electrochemical debromination is similar to the latter process involving an electron transfer and should therefore give similar products.

BDEs have also been shown to undergo partial metabolism in living organisms resulting in the formation of lower brominated diphenyl ethers as well as methoxy and hydroxy BDE derivatives. Debromination of BDE-209 has been reported in fish, including rainbow trout¹ and carp,¹¹ in rats,¹² in cows¹³ and in humans.¹⁴ Metabolic debromination of BDEs at the cellular level may occur through an electron transfer mechanism.^{15,16}

The objective of this work was to study the products formed from the electrochemical debromination of commercial DecaBDE (DE-83TM) in the presence of water. Experiments were also conducted in deuterated water and this gave some insight into the mechanism of debromination. The products generated are compared with those from previous work on the photolysis and metabolism of BDE-209.

2.0 Experimental

2.1 Electrolysis Experiments

The electrolysis experiments were performed in an undivided cell with fixed platinum black electrodes. DE-83TM (Great Lakes) was dissolved in freshly distilled THF (Aldrich) (ca. 1 mg/mL) containing

tetrabutylammonium perchlorate (Fluka), as supporting electrolyte (30 mmol/L), and water (HPLC Grade; Caledon) or D₂O (CDN Isotopes). A current of 20 mA was applied to the stirred solution resulting in a voltage of 20-26 V. Samples (50 µL) were withdrawn at the chosen time intervals. The samples were diluted with 3 mL hexane/10%DCM and eluted through a short silica plug to remove the supporting electrolyte. In order to quantitatively determine the BDEs using isotopic dilution, the samples were spiked with MBDE-MXE (¹³C₁₂-BDE surrogate mixture) before elution through the silica column. BDE-CVS-EISS (¹³C₁₂-BDE-138 injection standard) was added after the eluent volume was reduced and prior to injection on the HRGC/HRMS system. The BDEs were quantitated using a 5-point (BDE-CVS-E) calibration curve.

2.2 High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS).

The analyses were conducted on a HP6890 HRGC coupled to a Waters Autospec Ultima HRMS. The GC column was a J&W 30 m DB-5HT (0.25 mm ID, 0.1 µm film). The injections were done in splitless mode, with the injector temperature at 280°C and at a constant flow rate (helium) of 1.25 mL/min. The following temperature program was used: 100°C (3 min hold), 12°C/min to 280°C, 20°C/min to 325°C (10 min hold). The mass spectrometer was operated in selected ion monitoring (SIM) mode (EI+) at a resolution of at least 10,000 in each of five acquisition functions. The transfer line and source were maintained at 280°C. Perfluorokerosene-H was used as a calibration compound for the mass spectrometer.

3.0 Results & Discussions

In previous work,¹⁷ electrocatalytical hydrogenolysis gave efficient debromination for monobromodiphenyl ethers but was ineffective for higher brominated diphenyl ethers due to their poor solubility in aqueous methanol. THF was chosen as the solvent for this study due to its capability to more easily dissolve BDE-209. Since technical DecaBDE has higher solubility than BDE-209 in organic solvents due to the presence of impurities, the former was chosen as a substrate for the electrolysis experiments. The lower BDE congeners originally present in the DecaBDE were accounted for during the quantitation of the debrominated products after electrolysis.

Initial attempts to debrominate the DecaBDE in THF solutions containing 0.05% water required very high concentrations of supporting electrolyte to maintain a voltage with a reasonable current (20 mA). An increase of the water content to 2.5% allowed for a 20 fold reduction in the supporting electrolyte concentration.

Electrolysis of DE-83TM in THF in the presence of water resulted in the formation of di- through nona-bromodiphenyl ethers. Peak concentration of total octa-, penta- to hepta-, and tetra-BDEs were seen at time intervals of ten, twenty, and two hundred forty minutes, respectively (see Figure 1). The peak concentration versus time for the total nona-BDEs is difficult to determine as DecaBDE already contained these congeners. The data suggest that debromination is sequential but is very rapid under our conditions. The rates of debromination appear to be most rapid for the higher brominated congeners. Thus tetra- and tri-BDEs appear to be relatively much more stable to debromination by electrolysis. Since the mechanism probably involves an initial acceptance of an electron by the BDE molecule (ArBr) to form the radical anion ArBr^{•-}, it follows that the higher number of electronegative bromines on the ArBr makes it easier to accept an electron and proceed to debromination.

Once the radical anion is formed, it can form a radical complex by abstracting a proton from water followed by dissociation to a reduced product (ArH) and a bromine radical (Br^\cdot) (Figure 2, Path A). Alternatively, the radical anion $\text{ArBr}^{\cdot-}$ can lose bromide ion, Br^- , and the resulting aryl radical Ar^\cdot would abstract a hydrogen from the solvent, THF, to form the product (Figure 2, Path B) (there is also the possibility of reduction of the Ar^\cdot to Ar^- and a protonation). When the electrolysis experiments were conducted in the presence of D_2O , bromine was replaced exclusively by deuterium to give the lower brominated BDE congeners. This demonstrates that proton transfer involves exclusively water (Path A in Figure 2) and rules out a possibility of a hydrogen abstraction by Ar^\cdot .

The debrominated BDE products obtained from the electrolysis experiments are reproducible and not highly diverse indicating a specific favorable pathway (see Figure 3). The products obtained are similar to those observed in the debromination of BDE-209 in rainbow trout exposure,¹ except more products are seen in our experiments. It appears that BDE-47, BDE-99, and BDE-154 are not the major products of electrolysis at the time intervals when samples were taken. The identification of the unknowns is in progress.

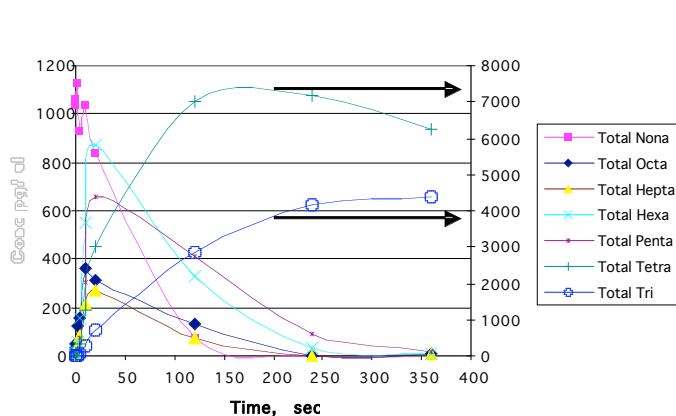


Figure 1. Products of DE-83 Electrolysis. Secondary Y-axis is the concentration of total Tri- and Tetra-BDEs in pg/ μL .

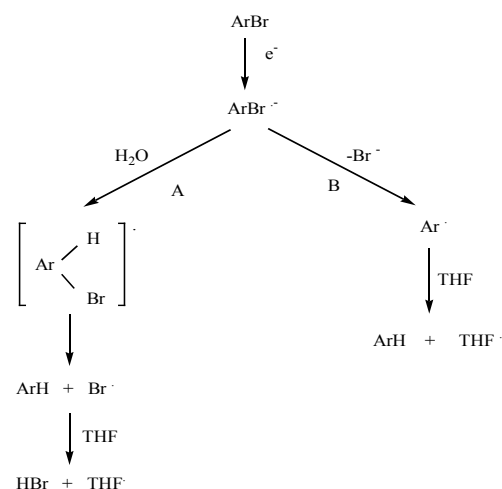
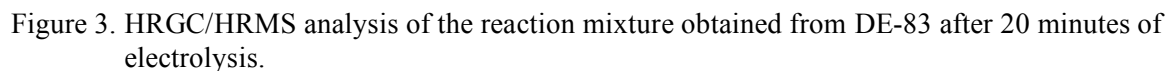


Figure 2. Mechanism of Debromination.



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